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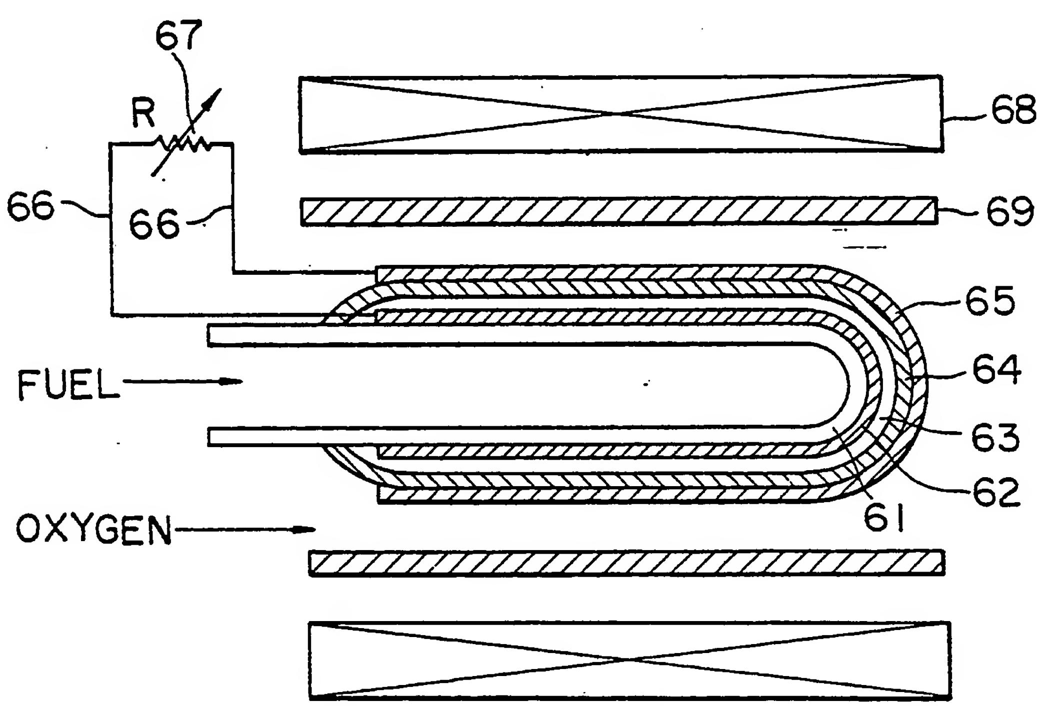
(54) **Solid electrolyte fuel cell and method for preparing it.**

(57) The present invention relates to a fuel cell that contains a solid electrolyte and provides a high-performance solid electrolyte fuel cell using a high-conductivity solid electrolyte, without a loss of output power due to a drop in the oxygen ion transport number.

The present invention is a solid electrolyte fuel cell which comprises many unit cells each in which a stabilized zirconia system solid electrolyte or a ceria system solid electrolyte containing an additive in such an amount or more as to exhibit a maximum value of conductivity is laminated on an anode side of a fundamental electrolyte, and a ceria system solid electrolyte is laminated on a cathode side thereof to form the solid electrolyte having two or more layers.

The present invention is utilized as a power source for various devices and appliances.

FIG. 3



Solid Electrolyte Fuel Cell and Method for Preparing It

The present invention relates to a fuel cell incorporated with a solid electrolyte and a method for preparing it.

Fuel cells which have been invented by Lord Grove in the first half of the nineteenth century are now at a practicable level after many changes and improvements.

The fuel cell is a kind of device for directly converting chemical energy into electrical energy, and its main constitutinal elements are an anode, a cathode and an electrolyte. As the electrolyte of them, an aqueous solution or a molten salt is usually used, but solid electrolyte fuel cells (i.e., solid oxide fuel cells; hereinafter referred to as SOFC) in which solid materials having an ionic electrical conductivity are employed have also made rapid progress in recent years. SOFC is also called the fuel cell of the third generation and has the following advantages, in contrast to a phosphoric acid type cell (the first generation) and a molten salt type cell (the second generation):

(1) A catalyst of a noble metal such as platinum is not required.

(2) An energy conversion efficiency is higher.

(3) A low-quality fuel such as a coal gas is also usable.

However, when the usual electrolyte such as a ZrO_2-CaO system material is used in SOFC, a necessary operation temperature is as high as 1,000°C and the selection of materials thus is difficult and troublesome.

The solid electrolyte fuel cell can convert chemical energy straightly into direct current energy. However, as described above, its required operation temperature is as high as about 700°C or more, generally about 1,000°C in order for the solid electrolyte to have a high conductivity. For this reason, the restriction on the materials is noticeably severe.

In the past days, a lot of electrolytes has been developed, but the conductivity of a stabilized zirconia, $(ZrO_2)_{0.85}(CaO)_{0.15}$, which is generally used in the fuel cell is 2.5×10^{-2} (Scm^{-1}) at 1,000°C. This value is not considered to be sufficiently high, and thus it is necessary that a wall thickness of the electrolyte is reduced, when used in the fuel cell. Further, the cerium system electrolytes having a good conductivity have been developed of late, but even in these cases, it is naturally needful to decrease their wall thickness.

As be definte from the above, since the conventional electrolyte in the fuel cell has no sufficient conductivity and since the operation temperature is high, the limitation on the materials is stern. Accordingly, the conventional solid electrolyte fuel cell is poor in performance and thus has the drawback that its operation is not easy.

Moreover, in the usual solid electrolyte fuel cell, the electrolyte on the side of a cathode thereof is in contact with moisture in an oxygen gas (or moisture in air, in the case that air is instead employed), and the electrolyte on the side of an anode thereof is in contact with produced water. As a result, when a CeO_2-CaO system or a ZrO_2-CaO system electrolyte is used, the following reaction will occur and CaO will be consumed, with the result that the fuel cell will deteriorate in performance disadvantageously:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Furthermore, in preparing the fuel cell, the electrolyte is required to be formed into a thin membrane, but in techniques for obtaining the thin electrolyte membranes such as a chemical vapor deposition (CVD) and an electrochemical vapor disposition (EVD), there are problems that facilities are too large and a treating ability per unit time is too low. That is why its industrialization is difficult inconveniently. Additionally, in the case of a usual powdery material for flame spraying, its cost is disadvantageously high, if in the form of a solid solution.

On the other hand, another type of electrolyte, for example, a ceria system (CeO_2-CaO, CeO_2-Gd_2O_3 or the like) electrolyte has a much higher conductivity as compared with the zirconia system electrolyte, and permits manufacturing the solid electrolyte fuel cell which can be operated at a relatively low temperature of 700 to 800° C. In such a ceria system electrolyte, however, a transport number of oxygen ions will drop in a zone in which a partial pressure of oxygen is low. In the case of the usual solid electrolyte fuel cell, the oxygen partial pressure n the side of a fuel electrode is very low (about 10^{-15} to about 10^{-30} atm), and thus the transport number of the oxygen ions in the solid electrolyte will fall, so that its output will deteriorate disadvantageously.

The object of the present invention is to provide a solid electrolyte fuel cell which comprises many unit cells each in which a stabilized zirconia solid electrolyte or a ceria system solid electrolyte containing an additive in auch an amount or more as to exhibit a maximum value of conductivity is laminated on an anode side of a fundamental electrolyte, and a ceria system solid electrolyte is laminated on a cathode side thereof to form the solid electrolyte having two or more layers.

The object, features and benefits of the present invention will be apparent from th following detailed

description in reference to drawings in which:

Figures 1 to 3 show the aspect of the present invention; Figures 1 and 2 are sectional views of the solid electrolytes used in the solid el ctrolyte fuel cells regarding the present invention, and Figure 3 is a constitutional view of a power generation test device for the solid electrolyte fuel cell of an embodiment regarding the tenth aspect of the present invention.

The invention is directed to a solid electrolyte fuel cell which comprises many unit cells each in which a stabilized zirconia system (ZrO_2-CaO system, ZrO_2-Y_2O_3 system or the like) solid electrolyte or cerium oxide (CaO_2) system solid electrolyte which contains an additive (CaO, SrO or the like) in such an amount or more as to exhibit a maximum value of conductivity and in which a transport number of oxygen ions does not drop even under a low partial pressure of oxygen is utilized on an anode side, and a ceria system (CeO_2-CaO, CeO_2-SrO or the like) solid electrolyte having a very high conductivity is utilized on a cathode side to form the solid electrolyte having two or more layers.

According to the solid electrolyte fuel cell described above, under usual conditions of operation, the drop in the transport number of oxygen ions due to the low partial pressure of oxygen is so small as to be negligible, and the solid electrolyte on the cathode side has a high conductivity. Therefore, a performance of the cell can be improved by constituting these electrolytes in the form of a multilayer.

The multilayer solid electrolyte membrane employed in the present invention can be manufactured by the use of a usual CVD process, EVD process or flame spraying process.

Now, an embodiment of the tenth aspect of the present invention will be described. For more clarification, two terms will be first defined as follows:

Anode side electrolyte: A solid electrolyte of stabilized zirconia system or a ceria system which contains an additive in such an amount or more as to exhibit a maximum value of conductivity and in which a transport number of oxygen ions is not lowered even under a low partial pressure of oxygen.

Cathode side electrolyte: A ceria system solid electrolyte having a very high conductivity.

A solid electrolyte used in a fuel cell regarding the present invention is, for example, an electrolyte comprising an anode side electrolyte 51 and a cathode side electrolyte 52 adhering to the anode side electrolyte 51, as shown in Fig.1.

In the fuel cell employing such a solid electrolyte, the drop in the transport number of oxygen ions due to the low partial pressure of oxygen does not occur on the anode side electrolyte 51, and since the cathode side electrolyte 52 has a high conductivity, the fuel cell employing the cathode side electrolyte 52 can maintain the high conductivity on the whole, whereby excellent cell properties can be obtained.

The solid electrolyte used in the fuel cell regarding the present invention is not limited to the structure shown in Fig.1 but may take another multilayer structure comprising an anode side electrolyte 53 having a high content of CaO, a middle electrolyte 54 having an intermediate content of CaO and a cathode side electrolyte 55 having a low content of CaO. Particularly in the case the CeO_2-CaO system, such a multilayer type solid electrolyte as shown in Fig. 2 can be easily prepared without any seam only by controlling feed rates of CeO_2 and CaO. The solid electrolyte in Fig. 2 can also provide the same functional effect as in the electrolyte shown in Fig.1.

For the purpose of confirming the effect of the solid electrolyte fuel cell regarding the present invention, current - voltage properties are measured in accordance with such an arrangement as shown in Fig.3.

First of all, a silver paste is applied in a thickness of about 10 µm onto a porous support 61 an end portion of which is closed, and calcination is then carried out to form a porous anode 62. Afterward, a stabilized zirconia having a composition of $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ is applied in a thickness of 60 µm onto the anode 62 by means of a plasma flame spraying process in order to form an anode side electrolyte 63. A ceria system electrolyte having a composition of $(CeO_2)_{0.8}(CaO)_{0.2}$ is then applied in a thickness of 140 µm onto the anode side electrolyte 63 by the plasma flame spraying process, thereby forming a cathode side electrolyte 64. Further, a cathode 65 having a thickness of about 10 µm is formed on the cathode side electrolyte 64 in the same manner as in the case of the anode 62. Afterward, the anode 62 and the cathode 65 of the thus prepared solid electrolyte fuel cell are connected to a variable resistance 67 by the use of lead wires 66, 66 of a platinum net and a platinum wire, respectively.

A heat-resistant ceramic pipe 69 is then inserted into an electric furnace 68, and the solid electrolyte fuel cell is further inserted into the heat-resistant ceramic pipe 69. A test of power generation is then carried out raising a temperature in the furnace up to 900°C and employing hydrogen as a fuel and air as an oxygen source in order to investigate current - voltage properties. The results ar set forth in Table1 .

In Comparative Examples 1B and 2B in Table1., $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ and $(CeO_2)_{0.8}(CeO)_{0.2}$ are employed alone respectively as electrolyte materials, and the solid electrolytes each having a thickness of about 200 µm are formed. For the solid electrolyte fuel cells in which the thus formed electrolytes are used, a test is carried out in th same arrangement as in Fig.3 . Th results are set forth in Table 1.

Table 1

	Current Density (mA/cm^2)		
	100	200	300
Comp. Example 1B	0.82 V	0.70 V	0.63 V
Comp. Example 2B	0.84 V	0.74 V	0.66 V
Example B	0.89 V	0.79 V	0.71 V

The results in the aforesaid table indicate that the solid electrolyte fuel cell of the Example B can provide a higher output than the cells of Comparative Examples 1B and 2B.

According to the present invention described above in detail, a drop in an oxygen ion transport number due to a low partial pressure of oxygen does not occur on the side of the anode. and since the solid electrolyte with a high conductivity is used, the solid electrolyte fuel cell having an excellent performace can be provided.

Claims

1. A solid electrolyte fuel cell which comprises any unit cells each in which a stabilized zirconia system solid electrolyte or a ceria system solid electrolyte containing an additive in such an amount or more as to exhibit a maximum value of conductivity is utilized on an anode side, and a ceria system solid electrolyte is utilized on a cathode side to form the solid electrolyte having two or more layers.

FIG.1

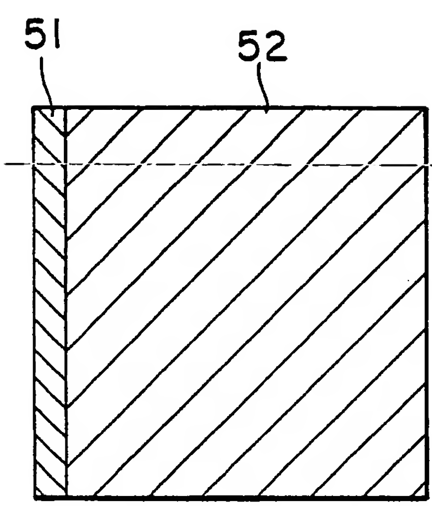


FIG.2

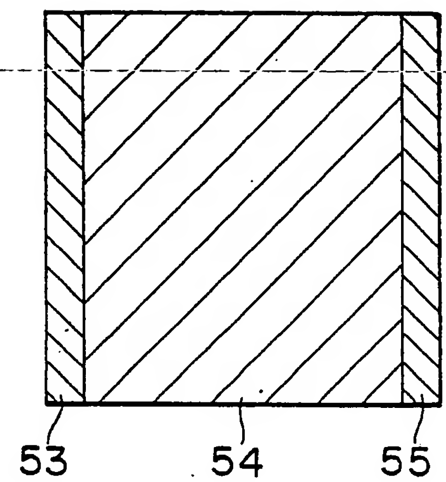
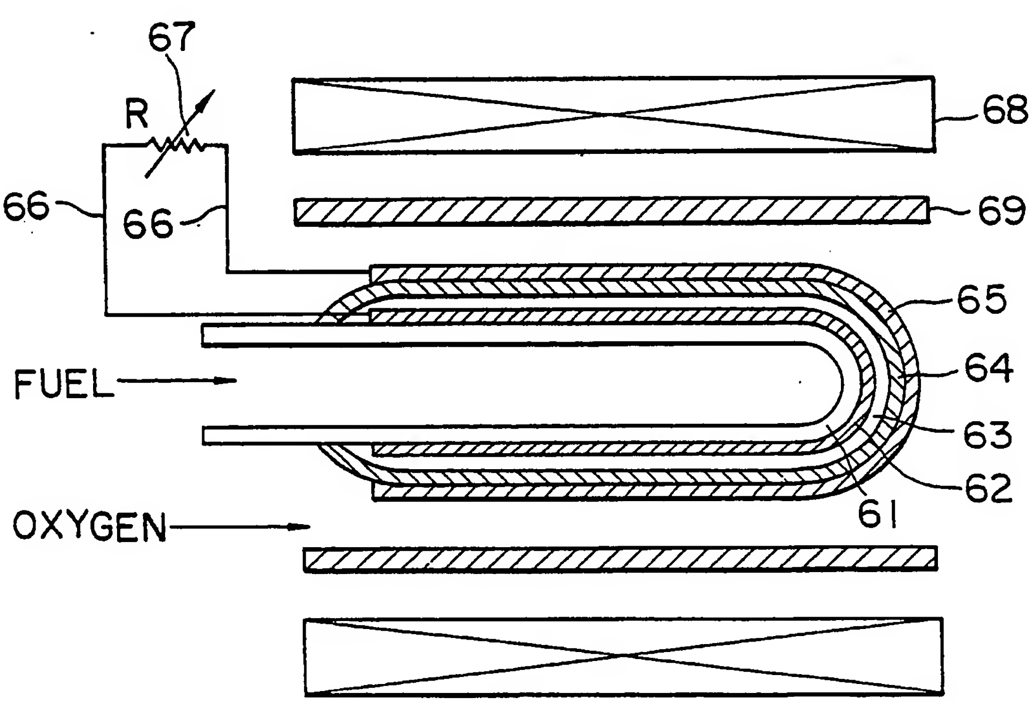


FIG. 3



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EUROPEAN SEARCH REPORT

Application Number

EP 87 11 1865

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	CHEMICAL ABSTRACTS, vol. 86, no. 2, 10th January 1977, page 91, abstract no. 7137j, Columbus, Ohio, US; & JP-A-75 12 566 (HITACHI LTD) 13-05-1975 * Whole abstract *	1	H 01 M 8/12
A	GB-A-2 027 729 (NISSAN MOTOR CO.) * Abstract *	1	
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 122, no. 2, February 1975, pages 255-259; H.L. TULLER et al.: "Doped ceria as a solid oxide electrolyte" * Page 255, left-hand column, paragraph 2; page 257, left-hand column, last paragraph *	1	
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 125, no. 8, August 1978, pages 1277-1282; D.S. TANNHAUSER: "The theoretical energy conversion efficiency of a high temperature fuel cell based on a mixed conductor" * Page 1277, right-hand column, paragraph 2; page 1278, left-hand column, paragraph 2 *		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
E	US-A-4 610 867 (T. SEIYAMA et al.) * Claims 1,5 *		H 01 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-02-1988	D'HONDT J.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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